Introduction to Nanotechnology

- Textbook：

  Nanophysics and Nanotechnology

  by:

  Edward L. Wolf

Instructor: *H. Hosseinkhani*
***E-mail:* hosseinkhani@yahoo.com**

Classroom: A209
Time: Thursday; 13:40-16:30 PM
Office hour: Thur., 10:00-11:30 AM or by appointment

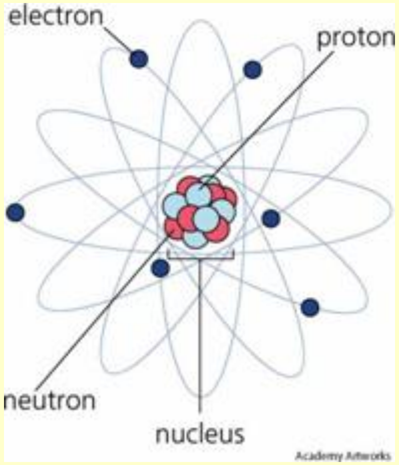
Physical-based Experimental Approaches to Nanofabrication and Nanotechnology-II

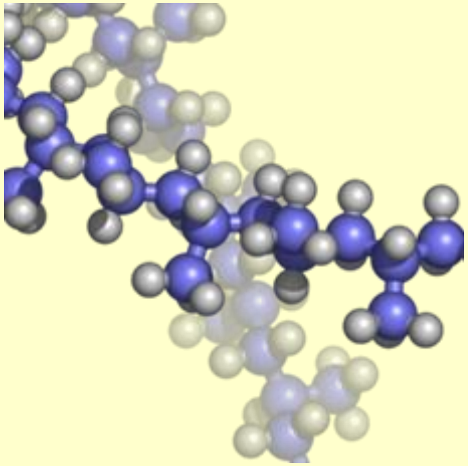
Subjects: Today class

1. Fabrication of Nanofibers
2. Application of Nanofibers in Industry

Key Dimensions in Nanometers

- An atom is about 0.3 nm in size.



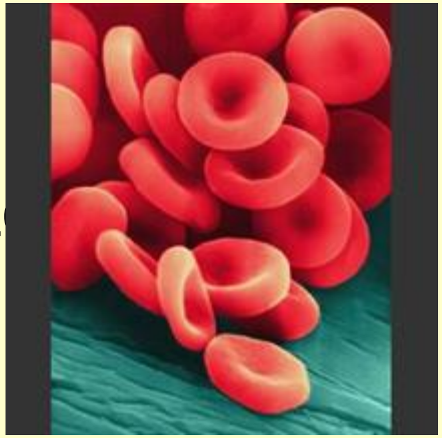


- Typical spacing between 2 carbon atoms in a molecule is 0.12 – 0.15 nm.

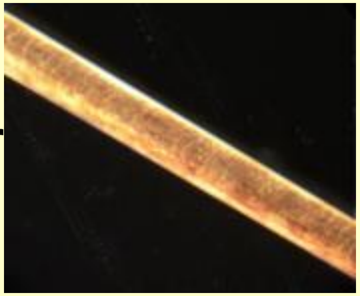
- DNA double helix has a diameter of about 2 nm.

- A bacterium of the genus Mycoplasma has a length of 200 nm.

- A red blood cell is 6,000 nm in diamet



- A human hair is 80,000 nm in diameter



- To put this scale in context, the size of a nanometer to a meter, is the same as that of a marble to the size of the Earth.

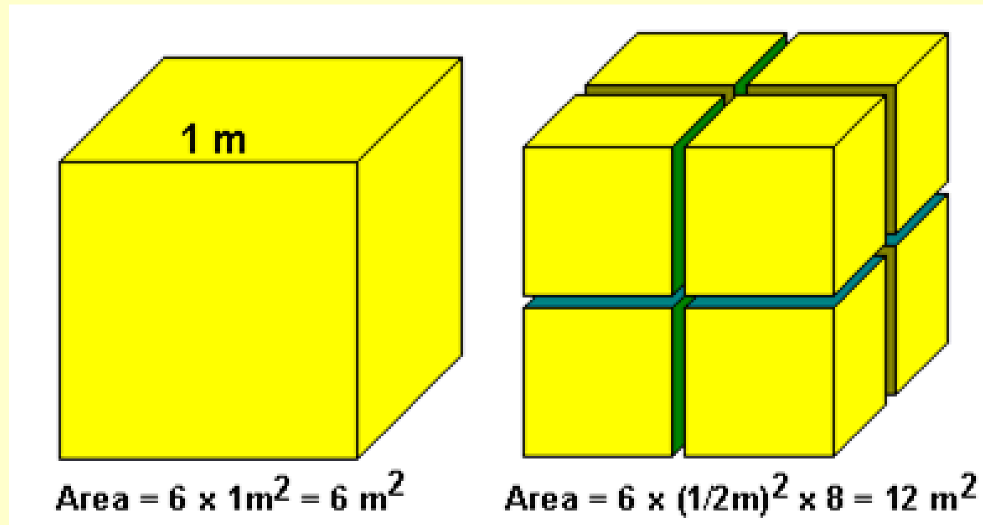
Model of Surface-to-Volume Comparisons…

Single Box Ratio

$$\frac{6\ m^2}{1\ m^3} = 6\ m^2/m^3$$

Smaller Boxes Ratio

$$\frac{12\ m^2}{1\ m^3} = 12\ m^2/m^3$$



- Neglecting spaces between the smaller boxes, the volumes of the box on the left and the boxes on the right are the same but the surface area of the smaller boxes added together is much greater than the single box.

Another Way to Think of this Ratio Using Sugar Cubes

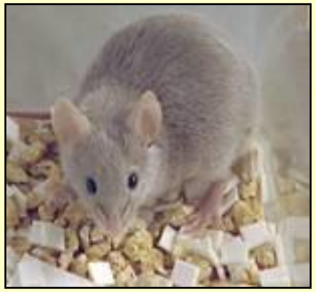
- Each individual cube is about 1 cm on a side, so each side has an area of 1 cm^2. With six sides, it has a surface area of 6 cm^2 and a volume of 1 cm^3.

  – This is a surface area to volume ratio of 6 cm^2/cm^3

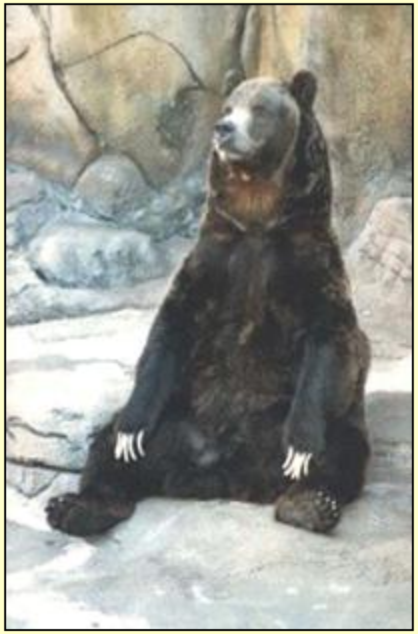
- A block made from 64 sugar cubes is 4 cm on a side and has a surface area of 6 x 16 cm^2 or 96 cm^2 and a volume of 64 cm^3.
  - This is a surface area to volume ratio of 1.5 cm^2/cm^3.

- If you compute the surface of all 64 individual cubes, you would have 64 x 6cm^2 or 384 cm^2 or 4 times more surface area with the same total volume.

An Example of the Affects of Surface-to-Volume Ratios in Animals

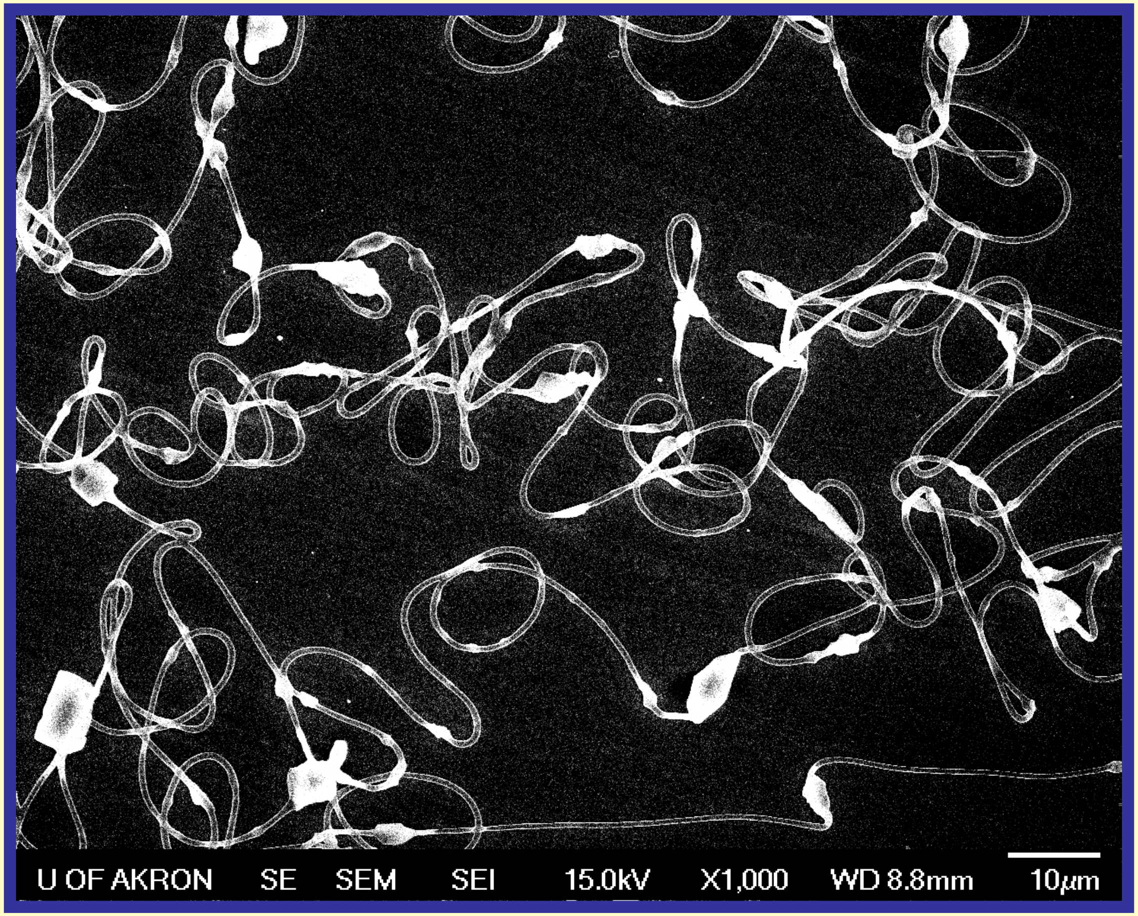


- Larger surface-to-volume ratio
  - Very susceptible to changes in heat



- **Smaller surface-to-volume ratio**
  - **Less susceptible to changes in heat**

Nanofibers:
What are they? Why are they important?



What is a Nanofiber?

- A nanofiber is a continuous fiber which has a diameter in the range of billionths of a meter.
- The smallest nanofibers made today are between 1.5 and 1.75 nanometers.
- At the right a human hair (80,000 nanometers) is place on a mat of nanofibers

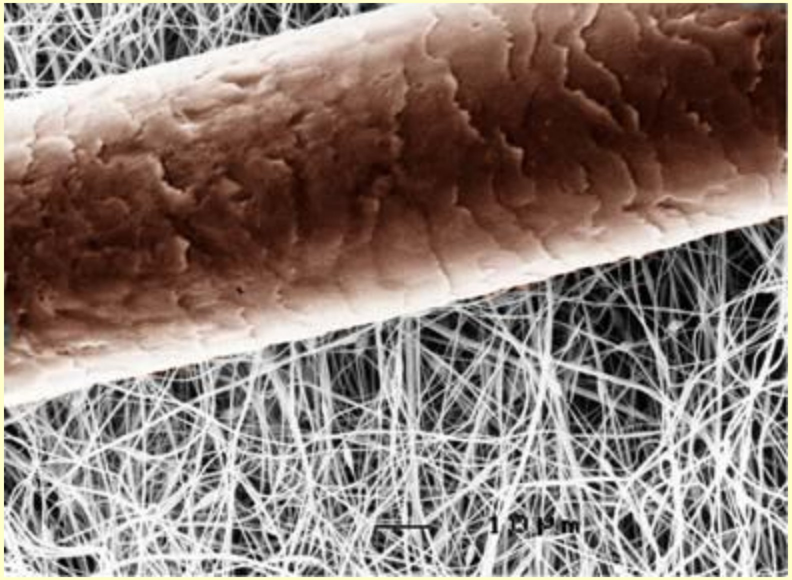
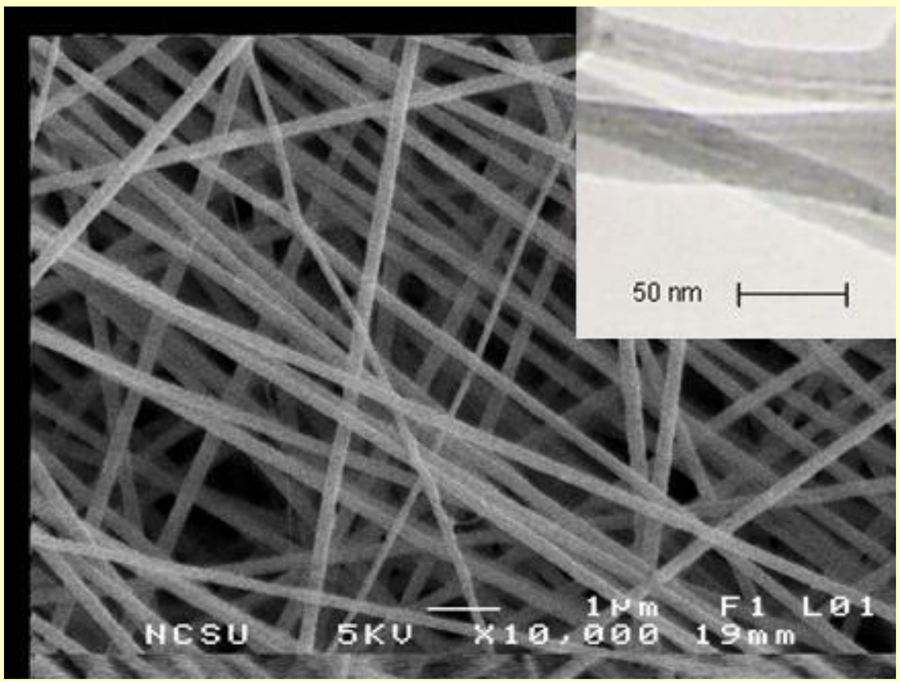


Image from EPA.gov

- Nanofibers range in diameter of 2-600 nanometers and are very difficult to see with the naked eye so they are studied using magnification…



Electron micrograph of nanofibers used for tissue scaffolds

Spider dragline 3,000 nanometers

Unique Properties of Nanofibers

- Size: nanofibers are very small which gives them unique physical and chemical properties and allows them to be used in very small places.

- Surface-to-volume ratio: nanofibers have a huge surface area compared to their volume. So scientists have lots of surface to work with!
  - The huge surface area available on a nanofiber makes it very suitable for new technologies which require smaller and smaller environments for chemical reactions to occur. Increasing the surface area speeds up a chemical reaction.

Making Nanofibers

Three different approaches toward the formation of nanofibrous materials have emerged:

1. self-assembly

2. electrospinning

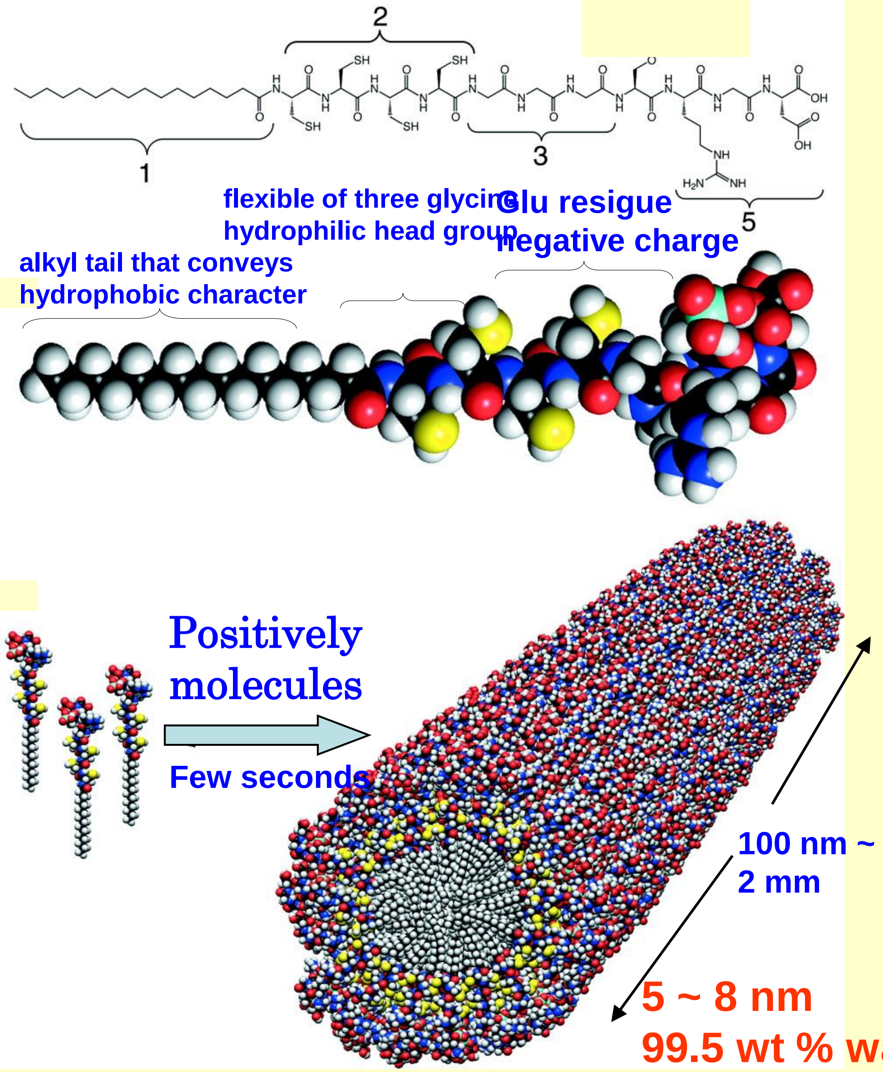
3. phase separation

Each of these approaches is very different and has a unique set of characteristics, which lends to its development as system.

1. self-assembly can generate small diameter nanofibers in the lowest range of natural materials. Self-assembly, that is, the autonomous organization of molecules into patterns or substrates without human intervention, are common throughout nature and technology. Self-assembly of natural or synthetic macromolecules produces nanoscaled supramolecular structures and nanofibers.

2. Phase separation, on the other hand, has generated nanofibers in the same range as natural materials and allows for the design of macropore structures.

3. Electrospinning has only generated large diameter nanofibers on the upper range of materials.



Peptide Amphiphiles can self assemble into sheets, spheres, rods, disks, or channels depending on the shape, charge, and environment

Amphiphiles with a conical shape in which the hydrophilic head group is somewhat bulkier than its narrow hydrophobic tail have been shown to form cylindrical micelles.
PA with mono- or di-alkyl tails were found to associate in conformations such as triple helical structures found in collagen.

High aspect ratio
High surface area

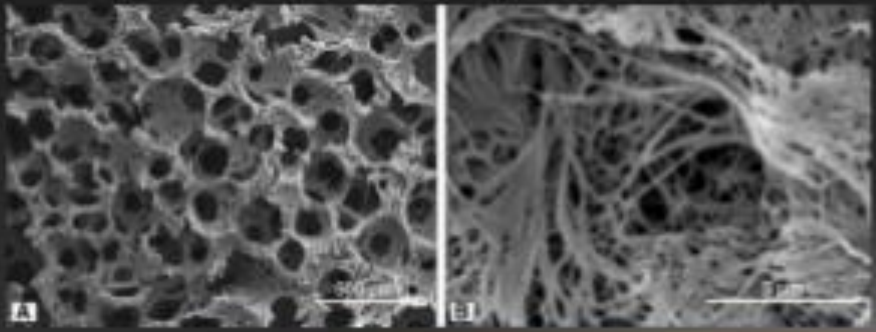
Cations can screen electrostatic repulsion among Peptide, and 3-D nonofiber are driven to assemble by hydrogen bond formation and electrostatic interactions, nonspecific van der Waals interactions, hydrophobic forces, and repulsive steric forces.

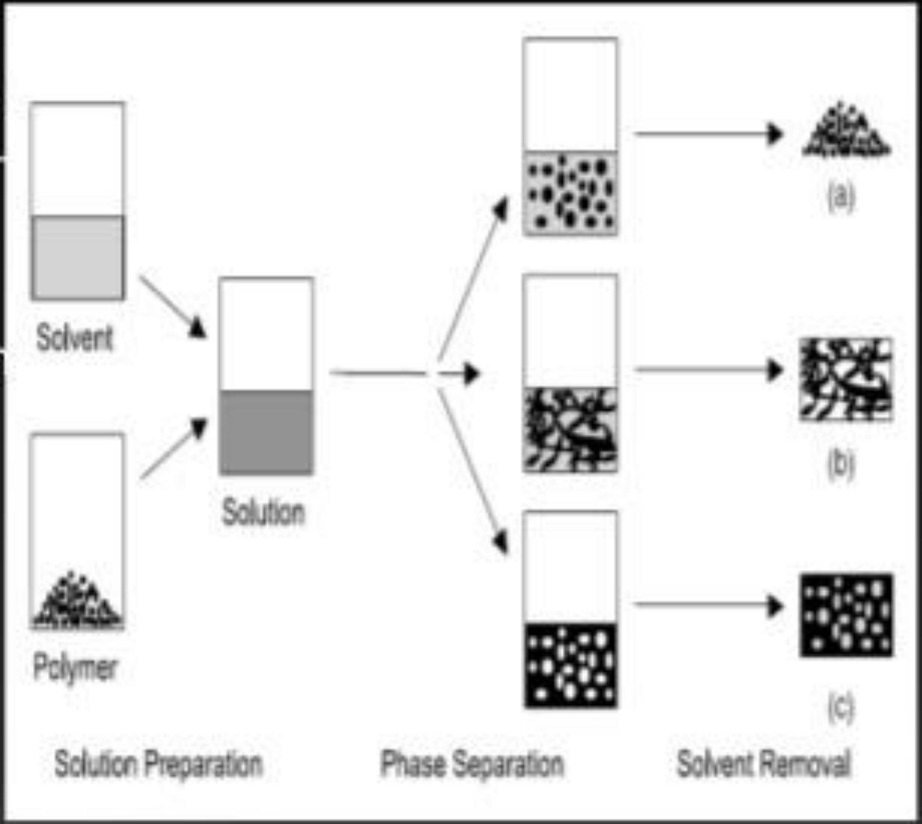
Ref: Science, Vol 303, 2004.

Phase Separation

Definition: thermodynamic separation of polymer solution into polymer-rich and polymer-poor layers

- This process involves dissolving of a polymer in a solvent at a high temperature followed by a liquid–liquid or solid–liquid phase separation induced by lowering the solution temperature
- Capable of wide range of geometry and dimension include pits, islands, fibers, and irregular pore structures
- Simpler than self-assembly





a) powder, b) scaffolds with continuous network, c) foam with closed pores.[4]

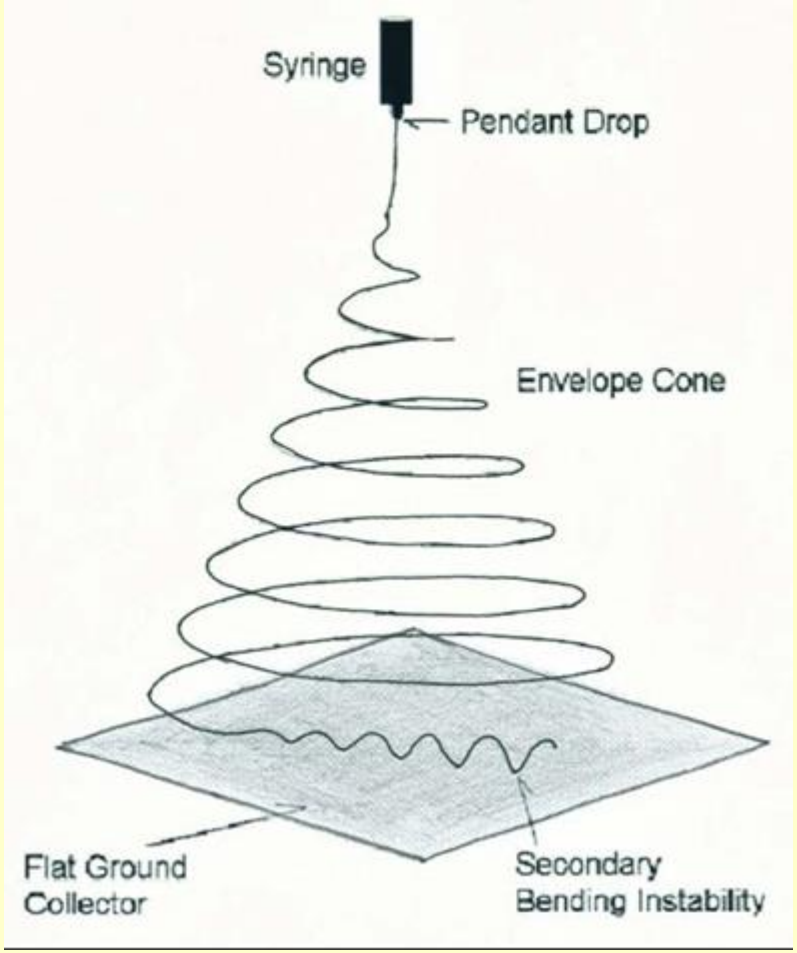
Making Nanofibers

"Melt" Fibers: some nanofibers can be made by melting polymers and spinning or shooting them through very small holes. As the fiber spins out it stretches smaller and smaller...

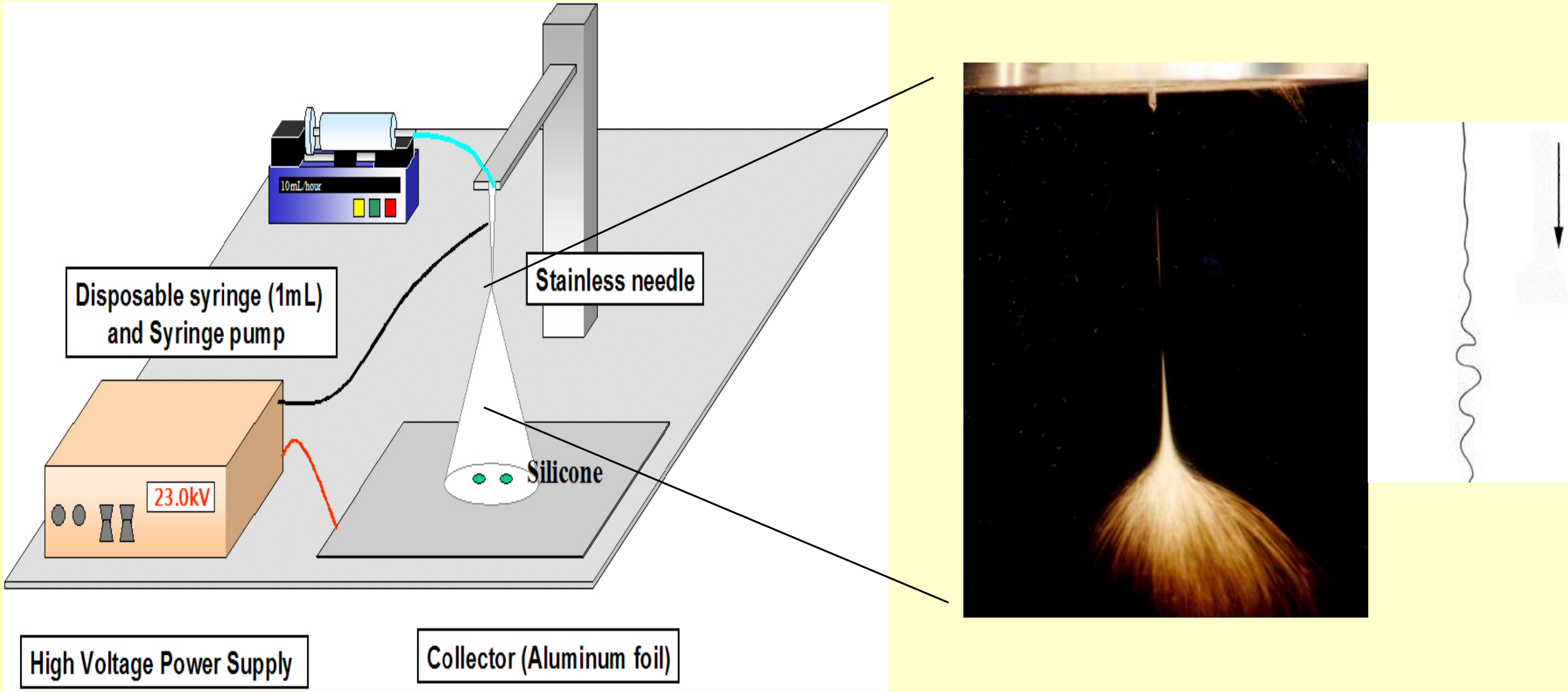
Cotton candy is made by heating syrup to a high temperature and then the liquid is spun out through tiny holes. As the fiber spins it is pulled thinner and thinner. It cools, hardens and, presto! Cotton Candy!!

Electrospinning to Make Nanofibers

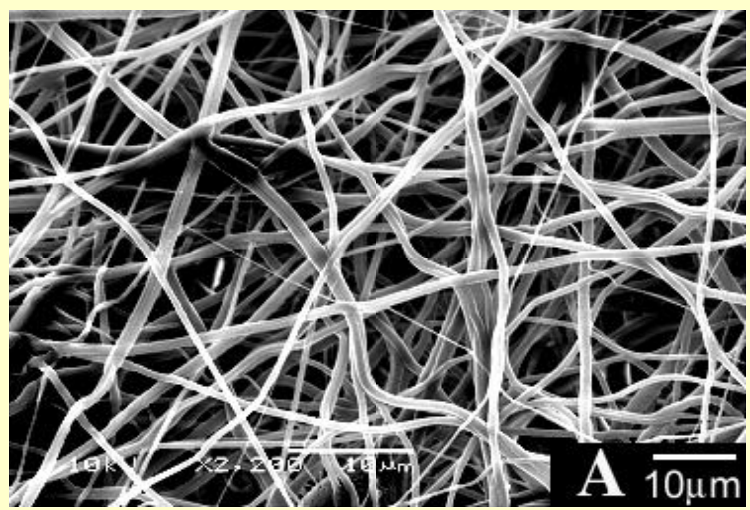
- An electric field pulls on a droplet of polymer solution at the tip of the syringe and pulls out a small liquid fiber. It is pulled thinner and thinner as it approaches the collection plate.



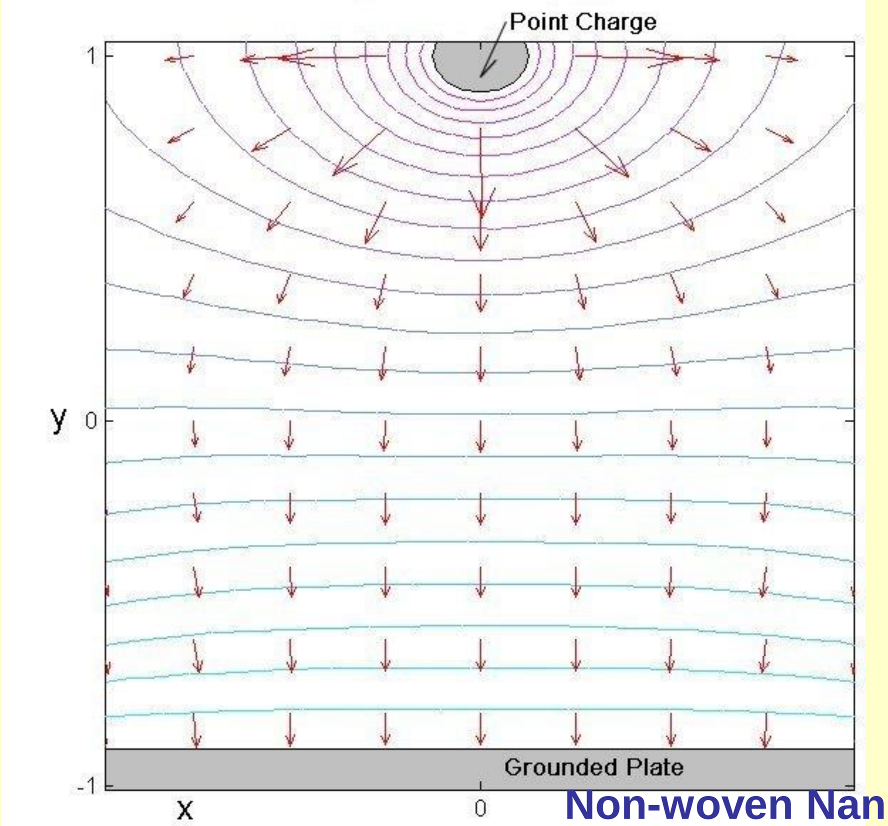
Electrospinning Apparatus



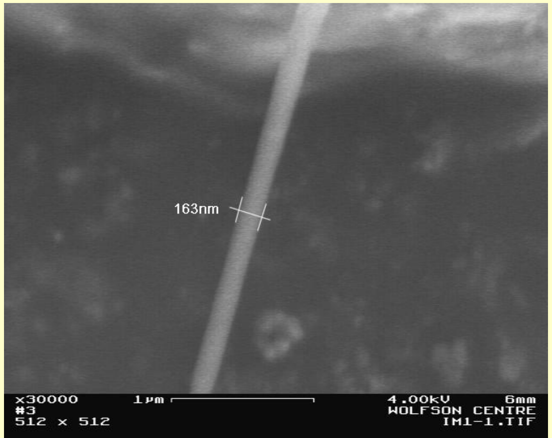
Random Nanofibers



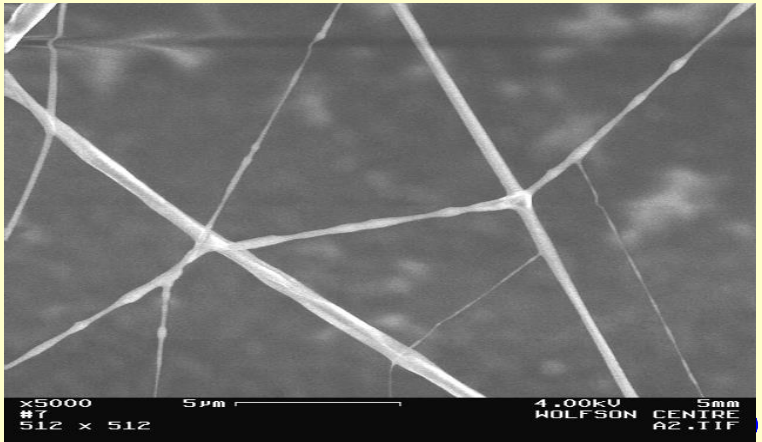
Equipotential Lines and Electric Field Lines in Electrospinning



Nanofiber (PEO)

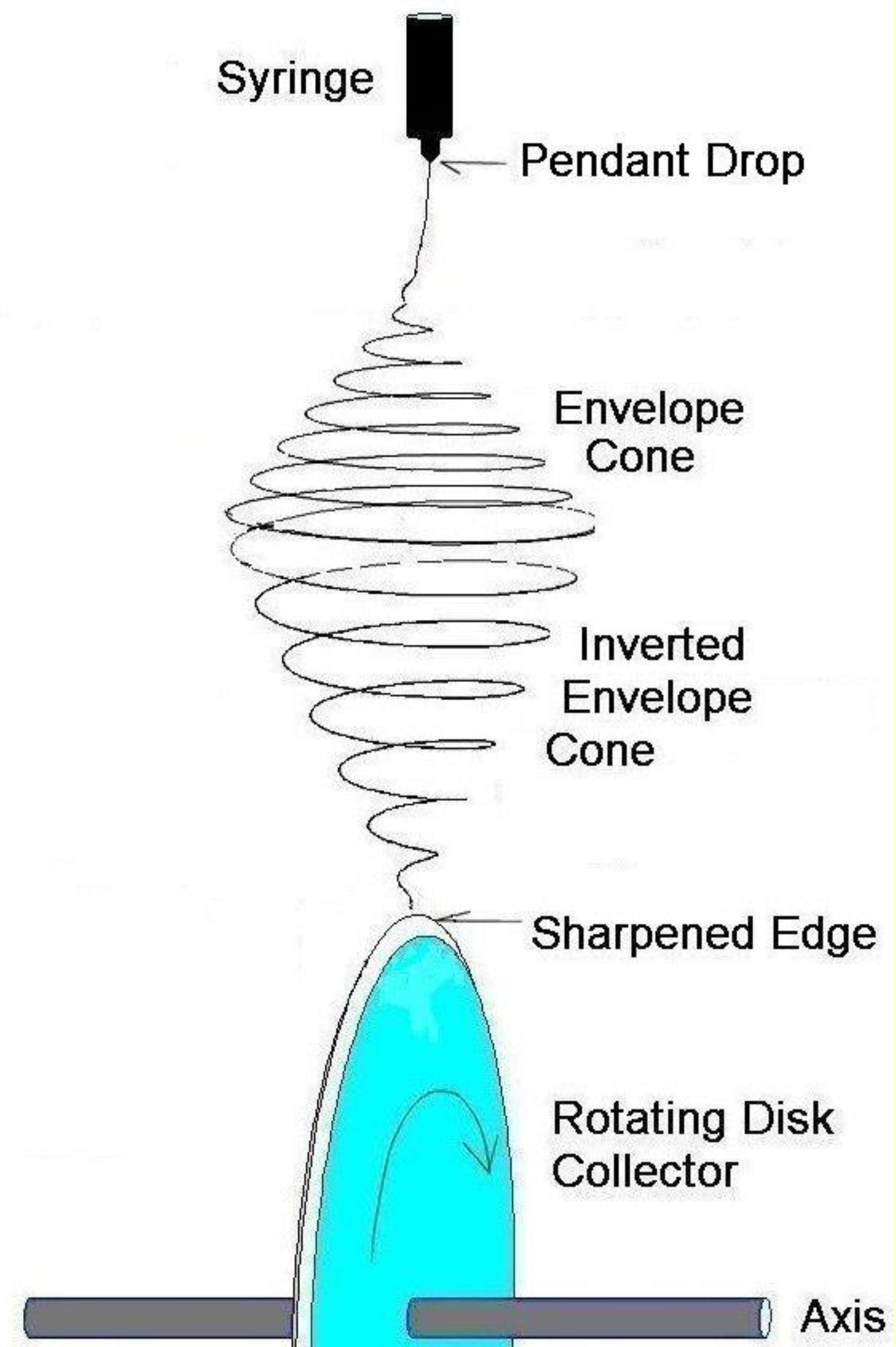


Non-woven Nanofiber Mat



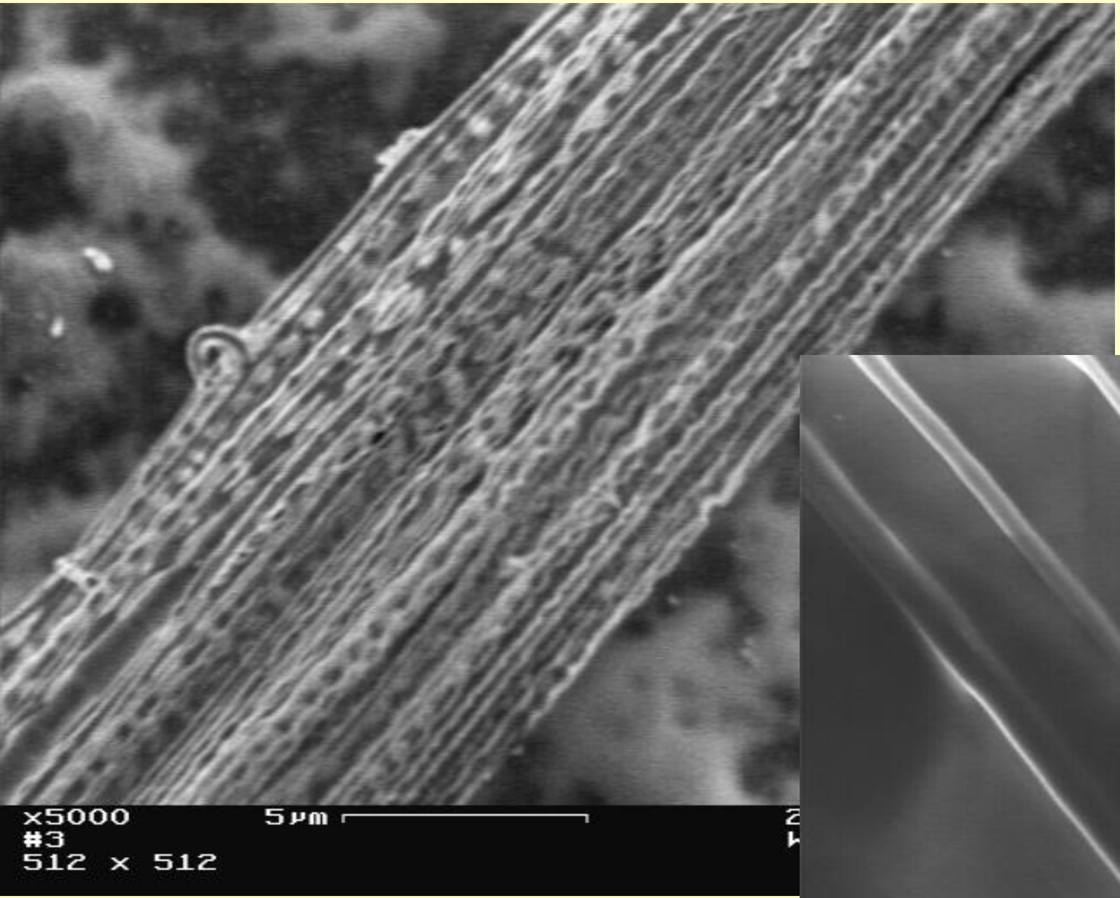
The Electrospinning Process:

Aligned Nanofibers

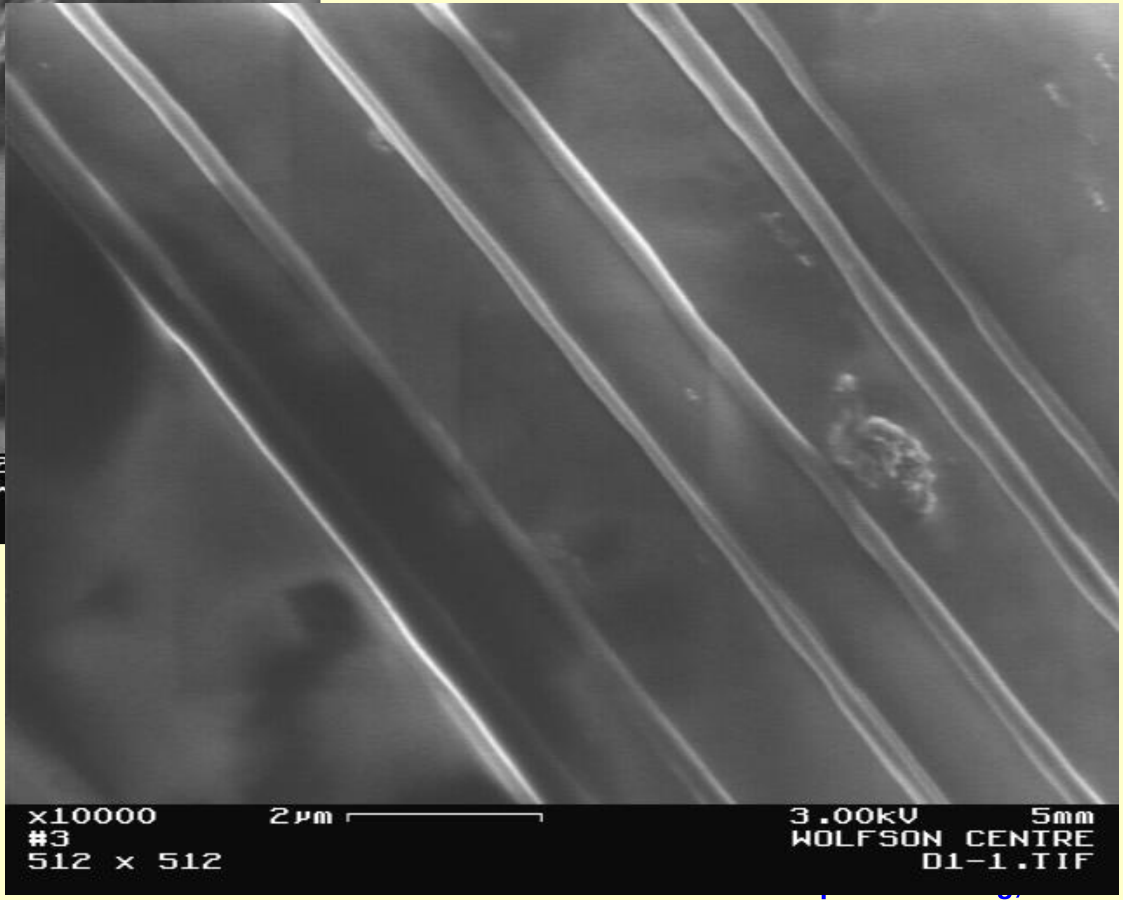


http://www.youtube.com/watch?v=zhZ2u_tZFP4

Braid of Aligned Nanofibers
Density≈100nfs/μm^2



Aligned Nanofibers



Electrospinning a Polymer Solution to Produce Nanofibers

- This picture shows the actual spinning of a solution made of the polymer PEO (polyethylene oxide) dissolved in water.
- Polymer solutions can be electrospun because of their long repeating units.
- The resulting fiber is collected below on a grounded plate

Image courtesy of Reneker Group
The University of Akron, College of Polymer Science

- Here you can see the individual fiber being pulled downward toward the grounded collection plate.

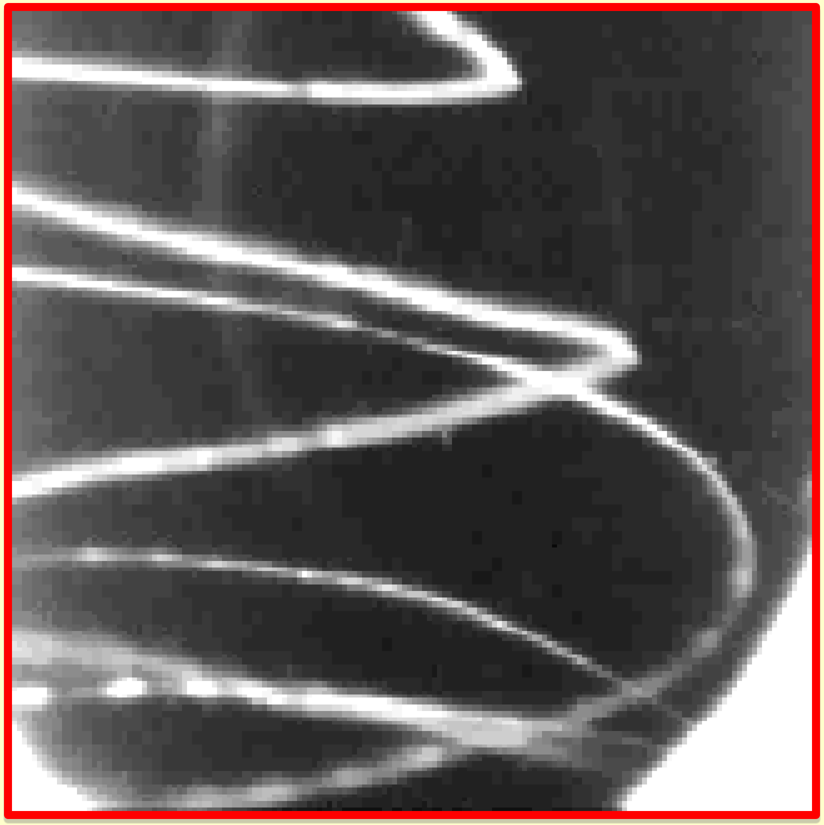
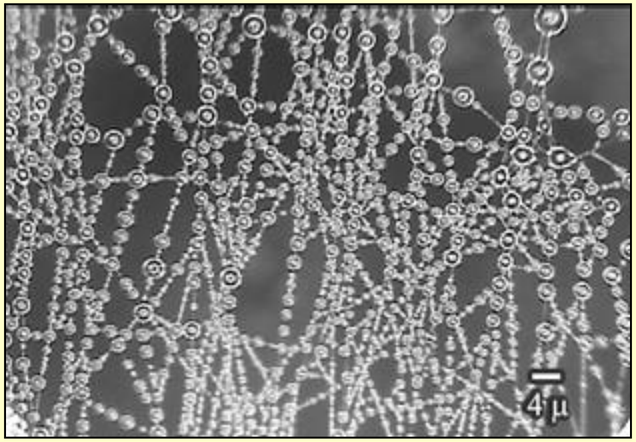


Image courtesy of Reneker Group
The University of Akron, College of Polymer Science

PEO (Polyethylene Oxide) Nanofibers

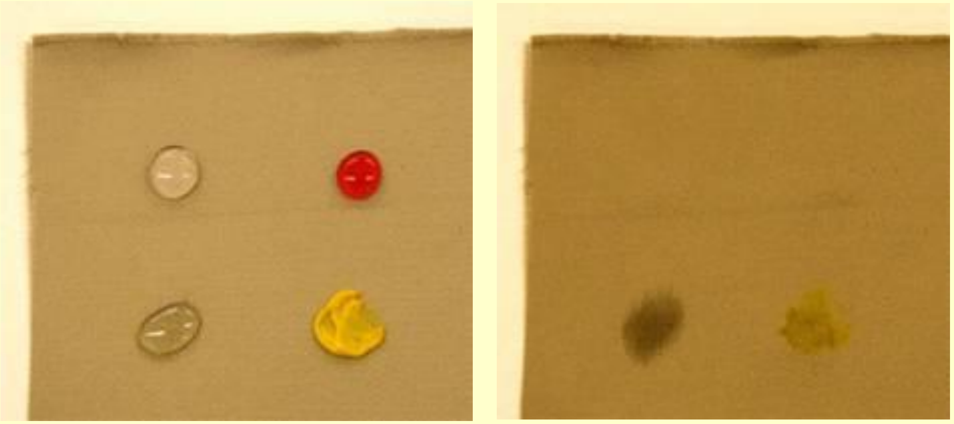
Uses of Nanofibers…

- High surface area: Filtration, Protective clothing.



Filter applications: Oil droplet coalescing on nanofibers increase the capture rate of the oil fog.

Nano-Tex fabrics with water, cranberry juice, vegetable oil, and mustard after 30 minutes (left) and wiped off with wet paper towel (right)



Uses of Nanofibers… continued.

- Support: Template for making different structures/coatings, catalysts/enzyme supports.
  - Tissue Scaffolding: Fibroblast cells grown on PLGA nanofibers.

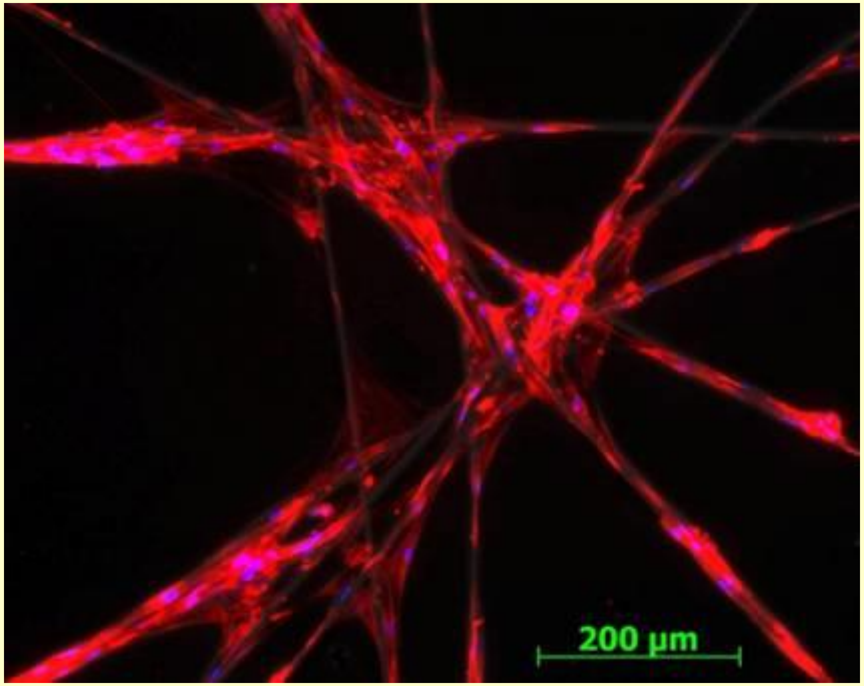


Image by Amy Liu, Hoover High School Student

Uses of Nanofibers… continued.

- Strength: Reinforced composites by nanofibers, twisted in yarns.
  - New yarns with outstanding wicking properties: Here electrospun nylon fibers are spun into yarns.

Image courtesy of Reneker Group –
The University of Akron, College of Polymer Science
and Samantha Loutzenheiser, Hoover High School.

Uses of Nanofibers… continued.

- Encapsulation: Drug delivery, Scaffolds for growing cells, Agriculture.
  - Water filtration: EDTA, a chelating compound, has been encapsulated in tecophilic nanofibers.
  - These fibers in a water filter can remove heavy metals, particularly lead, cadmium and copper.

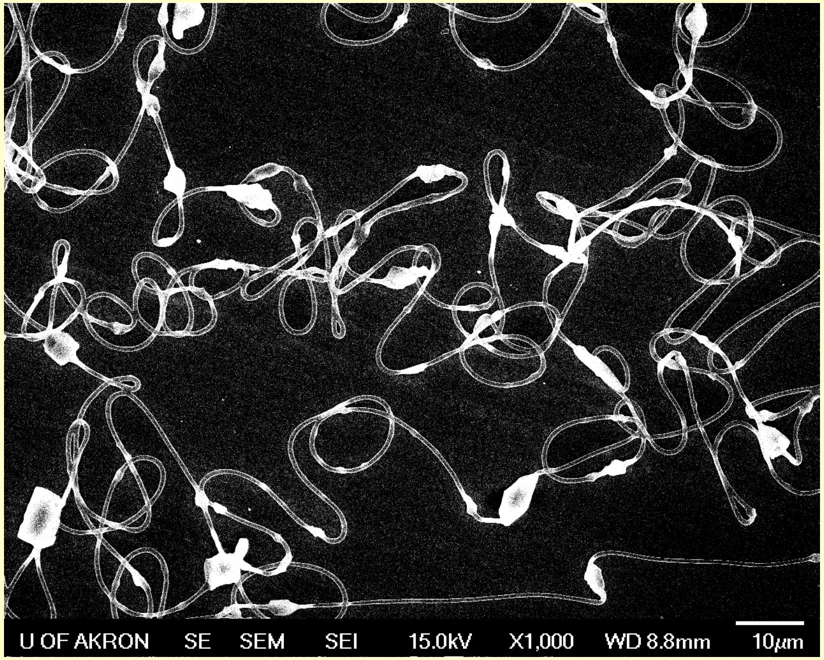


Image by Joe Sinha, Hoover High School Student

Uses of Nanofibers… continued.

- **Light Weight: Produce Solar sails in space, Aircraft wings, Bullet-proof vests.**
  - **New breathable bullet-proof vest: *Nomex* Nanofibers**

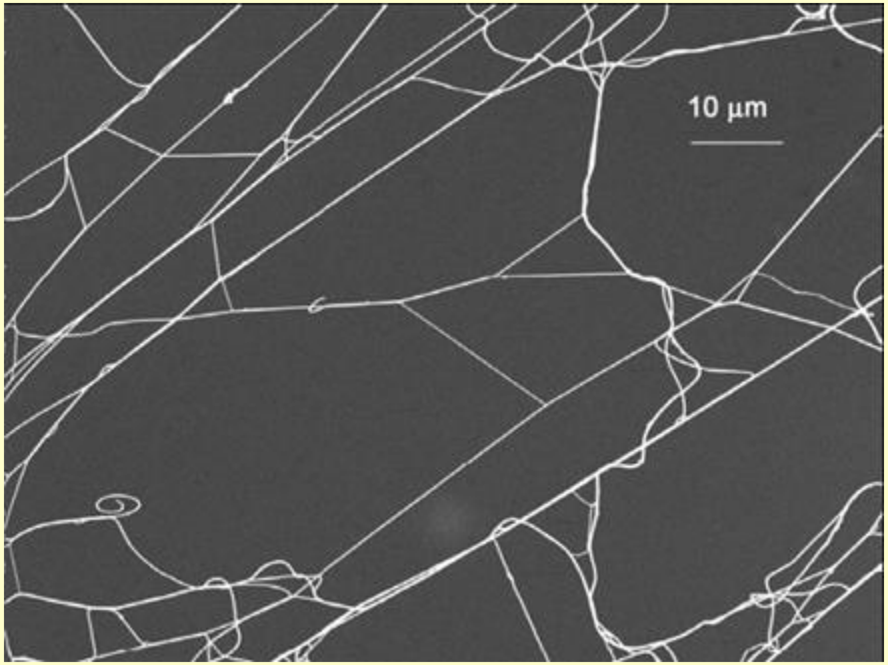
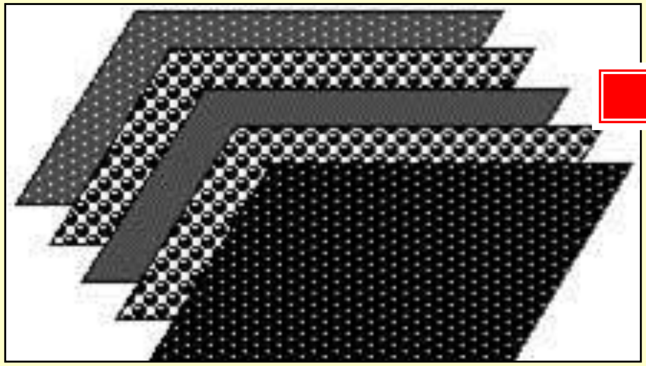
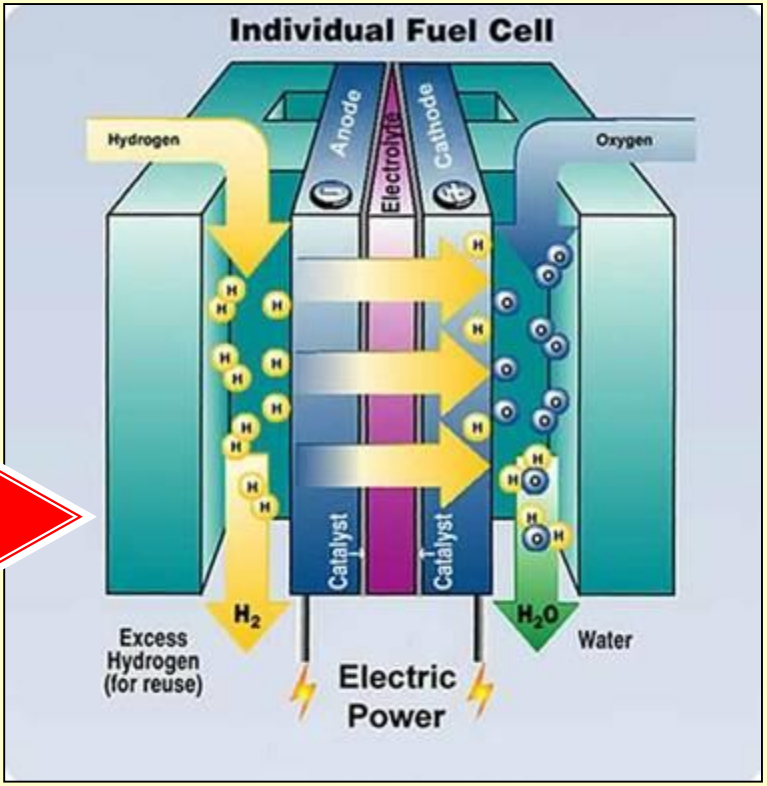


Image courtesy of Reneker Group –
The University of Akron, College of Polymer Science

Uses of Nanofibers… continued.

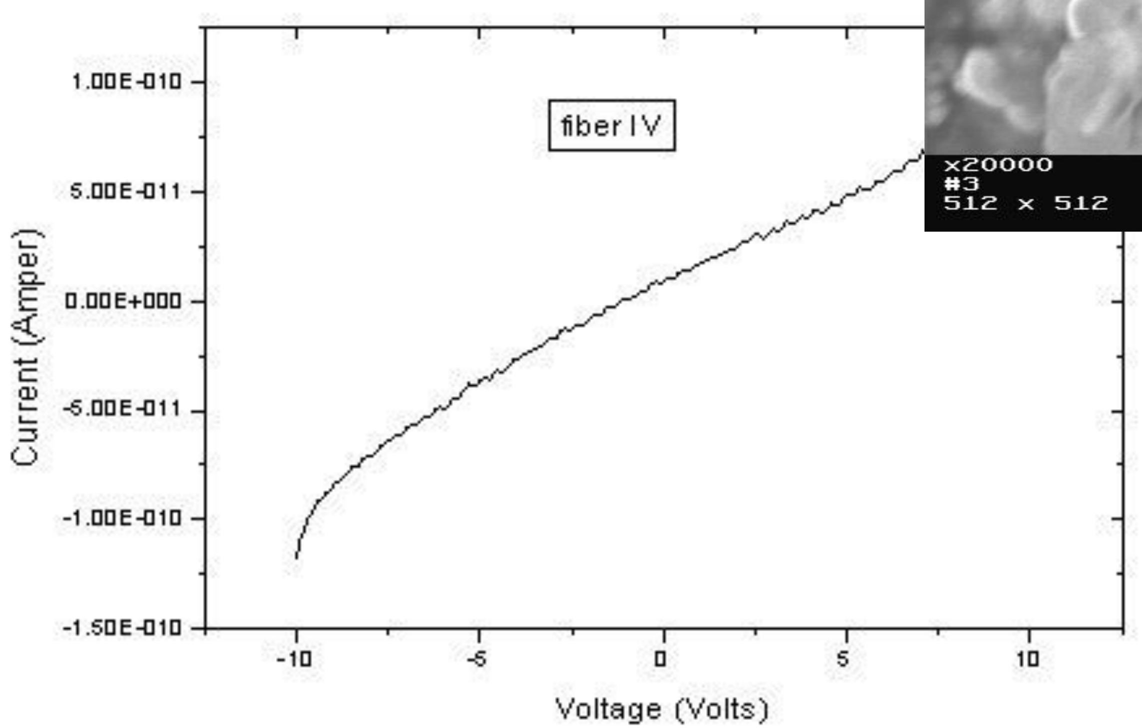
- Structure: Fuel cell, Micro/Nano electronic devices
  - Nanofibers can be used to greatly decrease the size of a fuel cell while increasing the electrical output.

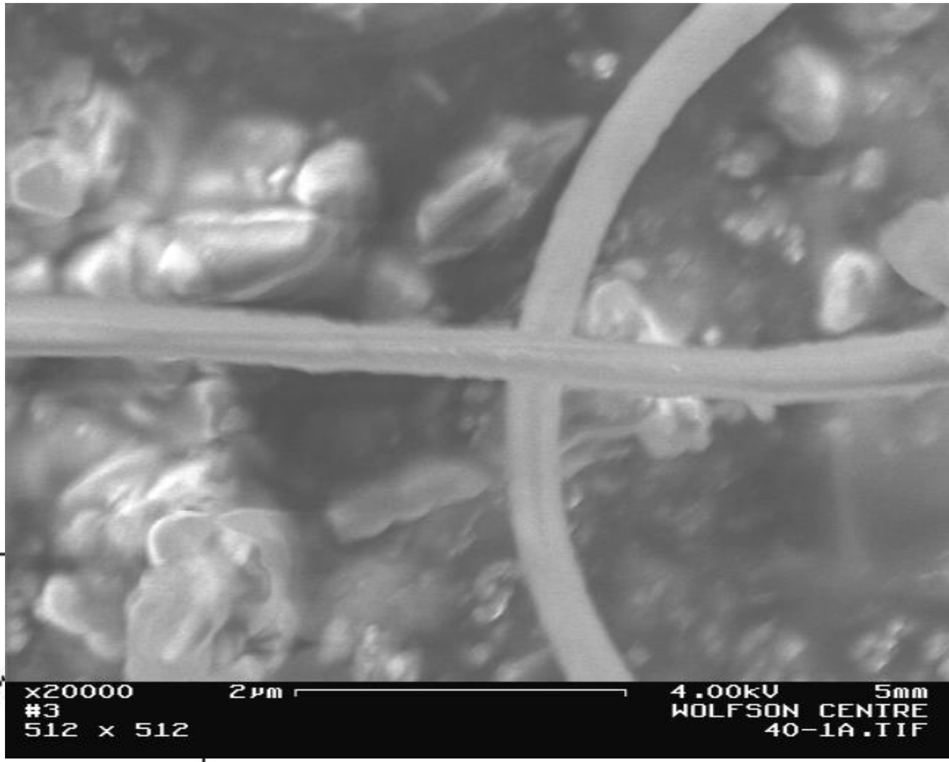




Conductive Nanofibers (PEDOT/PEO)

Current-Voltage Response





http://www.youtube.com/watch?v=qzvWESPG8Ho

Website Resources

http://www.nanitenews.com/

http://electrospun.blogspot.com/

http://micro.magnet.fsu.edu/primer/java/
scienceopticsu/powersof10/

http://www.nnin.org/edunews_6.html

Applications of electrospun nanofibres Filtration

Filtration

Filtration is necessary in many engineering fields. Fibrous materials used for filter media provide advantages of high filtration efficiency and low air resistance. Filtration efficiency, which is closely associated with the fibre fineness, is one of the most important concerns for the filter performance.

Protective clothing

The protective clothing in military is mostly expected to help maximize the survivability, sustainability, and combat effectiveness of the individual soldier system against extreme weather conditions, ballistics, and NBC (nuclear, biological, and chemical) warfare. In peace ages, breathing apparatus and protective clothing with the particular function of against chemical warfare agents such as sarin, soman, tabun and mustard gas from inhalation and absorption through the skin become special concern for combatants in conflicts and civilian populations in terrorist attacks.

Catalytic nanofibres

Chemical reactions employing enzyme catalysts are important in chemical processes due to their high selectivity and mild reaction conditions. Immobilised enzymes are used largely due to easiness of catalyst separation, enzyme stability, and their availability for continuous operations. The efficiency of these immobilised enzymes depends mainly on the pore structure and diffusion limitations of the substrate material. Nanomaterials are of recent interest as catalyst substrates due to their large surface area per unit mass and the feasibility for high catalyst loading.

Composite application

One of the most important applications of traditional (micro-size) fibres, especially engineering fibres such as carbon, glass, and Kevlar fibres, is to be used as reinforcements in composite developments. With these reinforcements, the composite materials can provide superior structural properties such as high modulus and strength to weight ratios, which generally cannot be achieved by other engineered monolithic materials alone. Needless to say, nanofibres will also eventually find important applications in making nanocomposites. This is because nanofibres can have even better mechanical properties than micro fibres of the same materials, and hence the superior structural properties of nanocomposites can be anticipated.

Electrical and optical application

Conductive nanofibres are expected to be used in the fabrication of tiny electronic devices or machines such as schottky junctions, sensors and actuators. Due to the well-known fact that the rate of electrochemical reactions is proportional to the surface area of the electrode, conductive nanofibrous membranes are also quite suitable for using as porous electrode in developing high performance battery. Conductive (in terms of electrical, ionic and photoelectric) membranes also have potential for applications including electrostatic dissipation, corrosion protection, electromagnetic interference shielding, photovoltaic device, etc.

Medical application

Nanofibres are also used in the medical applications which include, drug and gene delivery, artificial blood vessels, artificial organs, and medical facemasks. Electrospun biocompatible polymer nanofibres can be deposited as a thin porous film onto a hard tissue prosthetic device designed to be implanted into the human body. This coating film is expected to efficiently reduce the stiffness mismatch at the tissue interphase and hence prevent the device failure after the implantation. Nanofibres and webs are capable of delivering medicines directly to internal tissues. Anti-adhesion materials may be used for such applications. Nanofibre, spun from compounds naturally present in blood, can be used as bandages or sutures that ultimately dissolve into body. This nanofibre minimize infection rate, blood loss and is also absorbed by the body.